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INTERDIFFUSION AND GRAIN-BOUNDARY MIGRATION IN Au/Cu BILAYERS DURING ION-IRRADIATION

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ABSTRACT

Ion irradiation and annealing experiments have been conducted on Au/Cu bilayer films to evaluate the effect of irradiation on diffusion-induced grain boundary migration (DIGM). The Au films were prepared with a large-grained microstructure with grain boundaries perpendicular to the film surface and extending through the film thickness. Irradiations were conducted with 1.5 MeV Kr at 228°C. Rutherford backscattering spectrometry of the samples revealed that interdiffusion was substantially enhanced in the irradiated area relative to the unirradiated area. Both irradiated and annealed-only areas were characterized by a *nearly uniform* composition of 14 at.% and 7 at.% Cu respectively through the entire thickness of the underlying Au film. Small probe X-ray energy dispersive spectroscopy showed significant lateral compositional homogeneities in both irradiated and annealed areas. These two results are consistent with previous observations of DIGM in the Au/Cu system, suggesting that this previously unexamined interdiffusion mechanism contributes to ion beam mixing.

INTRODUCTION

Experimental ion beam mixing studies of bilayer metallic films have generally shown the existence of two temperature regimes [1]. In addition to a temperature-independent regime, a temperature-dependent regime typically begins near room temperature. The kinetic processes governing mixing in this thermally assisted regime are not well-understood. With few exceptions (for example ref.[2]), little effort has been made in evaluating the role of the initial microstructure of the films on subsequent mixing behavior in the temperature-dependent regime. One possible explanation, linking microstructural effects with enhanced mixing, is found in the phenomenon of diffusion-induced grain boundary migration (DIGM). DIGM, as summarized below, is an experimentally well-documented phenomena observed during low temperature (<300°C) thermal interdiffusion in a large variety of bulk and thin-film bilayer couples [3]. Experiments assessing its role during ion beam mixing, however, are essentially absent from the literature.

Fig. 1 schematically illustrates the DIGM process in a thin bilayer sample. During thermal annealing, solute atoms from film B diffuse into the grain boundary of film A, inducing boundary migration to occur. An A-B solid solution alloyed zone develops in the wake of this migrated boundary. In DIGM, grain boundary migration and atomic interdiffusion occur at temperatures well below those required for conventional thermal grain growth and bulk diffusion. While observations of thermally-induced DIGM are common, the mechanism and driving force for this phenomenon remain the subject of considerable debate [3].

In this study, we sought to examine the effect of ion irradiation on DIGM in Au/Cu bilayers. Previous experiments performed by Pan and Balluffi [4], and Grovenor [5], provide well-documented evidence of thermally-induced DIGM in Au/Cu bilayer films, and therefore the system provides a good basis for irradiation studies. Ion beam mixing studies in Au/Cu bilayers have also been previously performed [6,7]. The present work differs from previous studies in that the microstructure of the Au films, and the irradiation/annealing temperatures, were chosen to yield experimental conditions conducive to identifying DIGM.

Fig. 1. Schematic of the DIGM process.

EXPERIMENTAL

Bilayer couples of Au and Cu were electron-beam evaporated onto (100) single crystal polished MgO, and (100) cleaved NaCl, in a vacuum system with the pressure not exceeding 1×10^{-5} torr during Au deposition, or 3×10^{-6} torr during Cu deposition. Samples were prepared by first evaporating 580-700 Å of Au onto the substrates, followed by 160 Å of Cu onto the Au. The Au films were made with a large-grained ($\sim 0.26 \mu\text{m}$ diameter) polycrystalline microstructure; the grain boundaries were predominantly oriented perpendicular to the film surface and spanned the film thickness. DIGM has been demonstrated previously in thermal experiments [4] with samples of this microstructural type. Two procedures were followed to obtain the Au films. In the first method, Au was evaporated onto MgO and NaCl at room temperature and subsequently annealed at $\sim 450^\circ\text{C}$ for 1 hour. In the second method, Au was evaporated onto MgO held at 180°C during deposition. In both cases, the samples were cooled to room temperature prior to the deposition of the Cu overlayer.

1.5 MeV He Rutherford backscattering spectrometry (RBS) was used to analyze interdiffusion in the couples before, and after, irradiation and annealing treatments. Irradiations were performed at 228°C in the scattering chamber without breaking vacuum using 1.5 MeV Kr ions to doses $\leq 10^{15} \text{ cm}^{-2}$. The range minus straggling of the ions at this energy was beyond the Au/substrate interface. After achieving the desired dose, the samples were cooled at a rate $\sim 10^\circ\text{C}/\text{min}$ to room temperature. Both irradiated and unirradiated portions of the same sample were analyzed using RBS. RBS spectra were analyzed using RUMP [8].

Sample microstructure was examined by transmission electron microscopy (TEM) after floating the films from their substrates onto Mo TEM grids. Distilled H_2O was used to dissolve

NaCl substrates; a warmed solution of HCl was used to remove films from the MgO and etch away any remaining Cu film. X-ray energy dispersive spectroscopy (XEDS) in a Phillips CM-30 operated at 300 kV was used to identify average and local Cu concentrations in the etched films using both large ($>3\text{ }\mu\text{m}$ diameter) and small ($\leq 150\text{ }\text{\AA}$) electron beam probes, respectively.

RESULTS

Fig. 2 shows RBS results of interdiffusion typically observed for a bilayer sample. In the as-evaporated state, the sample consisted of $160\text{ }\text{\AA}$ Cu on $700\text{ }\text{\AA}$ of Au. Interdiffusion of the Cu in Au is apparent after irradiating and annealing at $228\text{ }^{\circ}\text{C}$. Two important observations are made from Fig. 2 regarding Cu diffusion into the Au film. First, the enrichment of Cu in the Au can be attributed to two contributions: (1) local enrichment near the Au/Cu interface, and (2) a nearly uniform enrichment of Cu extending through the entire thickness of the Au film. This uniform region is particularly evident over an $\sim 300\text{ }\text{\AA}$ thickness at the rear of the Au film. The second observation is that ion irradiation clearly enhanced both of these components. A factor of two increase in the uniform composition, from 7 to 14 at.% Cu, is observed after irradiation as determined by RUMP analysis of the spectra in Fig. 2.

TEM was performed on etched samples removed from MgO substrates after irradiation/annealing treatments and RBS analysis. A limited amount of small probe XEDS work demonstrated the presence of lateral compositional inhomogeneities. Attempts were made to probe the Cu concentration in grain boundary regions where DIGM may have occurred. However, in the irradiated regions, this was complicated by difficulty in identifying boundary regions due to the presence of irradiation damage. Probes were also placed at the center of grains which were easier to identify than boundary areas in TEM. The results for the sample whose RBS data is given in Fig. 2, along with large probe (film averaged) data, are summarized in Table I.

Selected area diffraction analysis of etched samples after irradiation and annealing showed only Au and solid solution Cu in Au. No ordered phases were detected.

DISCUSSION

RBS analysis of interdiffusion and XEDS observation of lateral compositional inhomogeneities subsequent to irradiation or annealing are consistent with the occurrence of DIGM in the Au films. The nearly uniform Cu tail observed in Fig. 2 results because a fixed volume fraction of the Au film becomes alloyed with Cu through the film thickness. The XEDS measured enrichment of Cu in Au boundaries ($\geq 20\text{ at.}\%$ Cu) is similar to the values (15-30 at.% Cu) measured previously by Pan and Balluffi in their thermal annealing experiments [4]. The annealing (RBS) results are comparable to those observed previously by Borders in an early study of thermal interdiffusion in Au/Cu bilayer films [9]. An important observation in his

Fig. 2. RBS data showing Au and Cu signals obtained from a Au/Cu bilayer on MgO. Irradiation and annealing performed at 228°C for ~40 min. Inset shows an enlargement of the Cu signal.

Table I. XEDS average Cu concentration (at.%) $\pm$ standard deviation (at.%) determined in irradiated and annealed-only regions of a Au/Cu bilayer treated at 228°C. Irradiation performed with 1.5 MeV Kr to a dose of 10^{15} cm $^{-2}$. The number of samples taken for each average are indicated in parenthesis.

Treatment	$\bar{C}$ -Large Probe (≥ 3 μ m diameter)	Small Probe (≤ 150 Å diameter)	
		C ₀ -Grain Center	C _B -Grain Boundary
Annealed-only	9.2 $\pm$ 2.9 (2)	4.0 $\pm$ 0.4 (3)	20.3 $\pm$ 0.2 (2)
Irradiated	16.7 $\pm$ 0.8 (4)	6.4 $\pm$ 0.5 (6)	24.6 $\pm$ 1.7 (4)

study was that negligible interdiffusion, with no uniform Cu enrichment, occurred for Cu in single crystal Au at 228°C. This demonstrated the importance of the Au microstructure (i.e. presence of grain boundaries) to interdiffusion.

Experiments by Akano et al. [2] on Ni-Pd bilayers suggested grain boundary diffusion as a possible mechanism for deeper penetration of solute in the solvent film. While grain boundary diffusion without DIGM may well be operative in our study, the magnitude of Cu enrichment observed in the Au film cannot be accounted for by this mechanism alone. Assuming a Au grain boundary width of 5 Å and complete Cu saturation of these boundaries, the Au must have a grain size on the order of 200 Å to achieve the smallest amount of uniform Cu enrichment (7 at.% for annealing-only) determined by RBS. This grain size is about an order of magnitude less than what is actually measured in the films (~0.26 μm). Borders [9] came to the same conclusion in his work but, prior to the discovery of DIGM, remained uncertain as to the source of the enrichment.

The combined results of RBS and small probe XEDS suggest the development of a Au film microstructure as depicted in Fig. 3. Using this figure, the extent of DIGM may be evaluated. For the analysis, it is assumed that the microstructure of the polycrystalline Au film may be modelled as a hexagonal array of grains of average width, L , whose boundaries are perpendicular to the film surface and extend through its thickness. After either irradiation or annealing, Cu interdiffusion takes place, both uniformly along the Au/Cu interface and via DIGM, as illustrated in Fig. 3. In the case of DIGM it is assumed that all grain boundaries migrate a distance, δ , producing a solid solution alloyed zone that has a Cu atomic concentration, C_B . Clearly this is an idealization, since not all boundaries are expected to migrate. However, δ , may be taken as the average over all migration distances. Interfacial mixing also contributes to enrichment of Cu in the Au, and this is specified by the composition C_0 . Both of these contributions contribute to an average Cu atomic composition, $\bar{C}$, as, for example, determined by a large XEDS probe. This analysis neglects any lateral interdiffusion induced by the ion beam between the DIGM alloyed zone and the adjacent grain.

Fig. 3. Idealized picture of DIGM and interfacial mixing occurring in the Au film of a Au/Cu bilayer subsequent to irradiation or annealing (Cu film removed).

Using simple geometric considerations, an expression may be derived relating the parameters shown in Fig. 3 and the film-averaged Cu composition, $\bar{C}$, which for $\delta \ll L$ becomes,

$$\frac{L}{2\delta} = \frac{C_B - C_0}{\bar{C} - C_0}. \quad (1)$$

Combining the values in Table I, and the measured grain size of $L \approx 0.26 \mu\text{m}$, the average distance of migrated boundary is estimated to be $\delta \approx 410 \text{ \AA}$ for annealed-only regions, and $\delta \approx 730 \text{ \AA}$ for irradiated regions.

As mentioned above, the mechanism of thermal DIGM is uncertain. One model suggests that a grain boundary Kirkendall effect occurs in the boundary of the solvent film [10]. Grain boundaries may be modelled as a series of stacked edge dislocations. If an unequal flux of solvent and solute atoms exists along these tilt

boundaries, dislocation climb is induced, resulting in boundary migration and a "freezing-in" of the composition in the boundary wake. A process can clearly be envisioned in which the presence of freely-migrating defects produced by irradiation kinetically affects either the boundary diffusivity and/or dislocation climb, in turn enhancing the DIGM process.

It is unclear to what degree DIGM may operate during irradiation of initially fine-grained bilayer films of the type typically used in ion beam mixing experiments. However, as the results of this work indicate, DIGM can enhance interdiffusion during irradiation at relatively low temperatures. Hence, the existence of this phenomenon may well impact on the interpretation of ion beam mixing results in the thermally-assisted regime. Additional irradiation studies are clearly warranted to evaluate this phenomenon.

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